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## C.1 Introduction<sup>1</sup>

The purpose of this appendix is to provide a general discussion of oil chemistry and the behavior of oil following an incident, including exposure and pathway information. Trustees may use this material when developing an inventory of possible injuries and evaluating the strength of evidence for these injuries, as described in Chapter 2. Trustees should recognize that the literature is extensive and growing rapidly and the information contained herein is subject to change. The information in this appendix is intended only to provide an overview.

In order to conclude that natural resource injuries resulted from the incident in the event of an actual discharge, trustees need to consider:

- The pathway(s) of the oil from the point of discharge to the injured natural resources;
- Whether injured natural resources were exposed, either directly or indirectly, to the same oil that was discharged;
- The geographical and temporal nature of the exposure; and
- Whether exposure to the discharged oil caused the injury.

Pathway and exposure information is important regardless of which NRDA procedure is selected. If a model-based assessment is conducted, pathway and exposure data may be the only incident- specific information collected.

As with other elements of the NRDA process, selection of appropriate strategies for evaluating oil pathways and exposure will depend upon the type and volume of spilled oil, natural resources at risk, and nature of the receiving environment. Early consideration of exposure and pathway issues (ideally during the Preassessment Phase) should help to focus the assessment on those natural resources that are most likely to be affected by a discharge. The following sections of this appendix provide a basic overview of oil chemistry and oil types, oil fates and weathering, mass balance estimates, pathways, and exposure considerations.

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<sup>1</sup> The text in this appendix was drafted by Douglas Helton, Damage Assessment Center, Seattle, WA.

## C.2 Oil Chemistry and Oil Types

The characteristics of discharged oil can provide the trustees with an initial screening of the potential pathways, exposure, and injuries resulting from the incident. However, the number and variability of crude and refined oils, each with different physical and chemical characteristics, makes such characterization daunting. For instance, fuel oils often are blended and the relative proportions of the component oils frequently change. Further, crude oils from different wells in the same region can have markedly different properties, and even the properties of oil taken from an individual well can vary with the depth of the well and the year of production (Bobra and Callaghan, 1990). Variability also exists within types or grades of oil. Therefore, the trustees need to access specific sources (i.e., databases) to simplify their task of characterizing oil in an adequate fashion. One such source is NOAA's Automated Data Inquiry for Oil Spills (ADIOS) database, which lists approximately one thousand different oils (NOAA, 1994a).

### C.2.a Oil Chemistry

Oils are complex mixtures of organic compounds and trace elements. Carbon (82-87%) and hydrogen (11-15%) are the most common elements of petroleum, with sulfur (0-8%), nitrogen (0-1%) and oxygen (0-0.5%) as important minor constituents (Duckworth and Perry, 1986). Trace elements vary widely and may include vanadium, nickel, iron, aluminum, sodium, calcium, copper, and others (National Research Council, 1985).

Oils typically are described in terms of their physical properties (e.g., density, pour point) and chemical composition (i.e., percent composition of various petroleum hydrocarbons, asphaltenes, and sulfur). Although very complex in makeup, these oils can be broken down into four basic classes of petroleum hydrocarbons: alkanes, naphthenes, aromatics and alkenes. Each class is distinguished on the basis of molecular composition, as described below.<sup>2</sup>

**Alkanes** (Also called normal paraffins): Alkanes are characterized by branched or unbranched chains of carbon atoms with attached hydrogen atoms and contain only singly carbon-carbon bonds (i.e., they are saturated, since they contain no double or triple bonds). Common alkanes include methane, propane, and isobutane.

**Naphthenes** (Also called cycloalkanes or cycloparaffins): Naphthenes typically comprise about 50% of the average crude oil. Naphthenes are similar to alkanes, but are characterized by the presence of simple closed rings of carbon atoms. Naphthenes are generally stable and relatively insoluble in water. Common naphthenes include cyclopropane and cyclopentane.

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<sup>2</sup> The following discussion is based on Fingas et al., 1979; Duckworth and Perry, 1986; Clarke and Brown, 1977; and National Research Council, 1985. The reader should refer to these documents for further information.

**Aromatics:** Aromatics are a class of hydrocarbons characterized by rings with six carbon atoms. Aromatics are considered to be the most acutely toxic component of crude oil, and are also associated with chronic and carcinogenic effects. Many low-weight aromatics also are soluble in water, increasing the potential for exposure to aquatic resources. Aromatics are often further distinguished by the number of rings, which may range from one to six. Aromatics with two or more rings are referred to as polycyclic aromatic hydrocarbons. Common aromatics include benzene, naphthalene, and benzo(a)pyrene.

**Alkenes** (Also called olefins or isoparaffins): Alkenes are characterized by branched or unbranched chains of carbon atoms, similar to alkanes except for the presence of double bonded carbon atoms. Alkenes are not generally found in crude oils, but are common in refined products, such as gasoline. Common alkenes include ethene and propene.

**Other Components:** In addition to these four major classes of hydrocarbons, oils also are characterized by other components. Asphaltenes and resins can comprise a large fraction of crude oils and heavy fuel oils, making those oils very dense and viscous. Other non-hydrocarbons that incorporate nitrogen, sulfur, and oxygen (also referred to as NSO) are also common. Crude oils that are high in sulfur are referred to as "sour."

- **20-200 °C:** 4-12 carbons: Straight-run gasoline (e.g., not produced through catalytic decomposition).
- **185-345 °C:** 10-20 carbons: Middle distillates, including kerosene, jet fuels, heating oil, diesel fuel.
- **345-540 °C:** 18-45 carbons: Wide cut gas oils, including light lube oils, heavy lube oils, waxes, and catalytic feed stock for production of gasoline.
- **>540 °C:** >40 carbons: Residual oils, which may be cut with lighter oils to produce bunker oils.

Refined oils also may have a number of additives (e.g., gelling inhibitors) that are added to diesel fuels during cold weather. Certain additives may be of special concern in an injury assessment, either because they are toxic themselves or because they significantly change the behavior of the oil.

## C.2.b Oil Types and Behavior

An understanding of the likely physical and chemical behavior of the discharged oil will help to focus the assessment on the most important injuries. For example, one of the most important factors in minimizing the shoreline impacts of the 1993 *Braer* incident in the Shetland Islands was the type of discharged oil (Harris, 1995). Norwegian Gullfaks crude oil has a low viscosity and relatively high degree of natural dispersion and, when combined with high wave energy, tends to disperse. Most of the oil from the *Braer* dispersed into the water column or broke into thin sheens within the first two days of the discharge and shoreline injuries were minimal. If the *Braer's* cargo had been a heavier crude, shoreline injuries would have been significantly greater.

There are a number of oil properties that should be considered when developing hypotheses about the potential for injury, including:

- Density;
- Viscosity;
- Pour point;
- Solubility;
- Chemical composition (especially percent aromatics); and
- Potential for emulsification.

These properties, combined with environmental information (e.g., water density, wave height, wind speed, currents, temperature, suspended sediment load, and cloud cover) and response efforts (i.e., use of chemical dispersants, and other countermeasures) can help to determine the fate of the discharged oil and natural resources that may be at risk.

Despite the variability noted by Bobra and Callaghan (1990), oils can be divided into six broad classes based on the predicted short-term behavior and likely injuries to natural resources. Pertinent properties of each oil class are summarized in Exhibit C-1 (RPI, 1994; NOAA, 1994b; Duckworth and Perry, 1986).

### C. 3 Oil Fates and Weathering

After oil is discharged into the environment, a wide variety of physical, chemical, and biological processes begin to transform the discharged oil. These processes are illustrated schematically in Exhibit C.2. Collectively, these processes are referred to as weathering and act to change the composition, behavior, routes of exposure, and toxicity of the discharged oil. For example, penetration into marsh vegetation may depend on oil viscosity. Weathered oils penetrate less than fresh oil (NOAA, 1992a). Weathered oil is composed of relatively insoluble compounds and often coalesces into mats or tarballs. As a result, the potential for exposure to fish through water column toxicity is lessened, as is the potential for birds or mammals to encounter the oil. Alternatively, certain species are known to ingest tarballs and the potential for exposure of those species may increase as the oil weathers (Lutz and Lutcavage, 1989, Gitschlag, 1992). Also, the loss of the lighter fractions through dissolution and/or evaporation during the weathering process can cause normally buoyant oil to sink, thereby contaminating subtidal sediment and contributing to water column toxicity (Burns et al., 1995; Michel and Galt, 1995).

Understanding the weathering process is important in interpreting oil samples. Constituents of the oil provide a chemical "fingerprint" that can be used to help identify or distinguish oil from a specific incident from other discharges, biogenic and pyrogenic sources, or background contamination. These constituents will vary depending on the geologic source of the oil and refinery process. In fingerprinting, the presence and relative concentration of specific constituents of the oil are compared with known source samples. Although fingerprinting focuses on constituents that are dominant constituents of the oil or that may be persistent, these constituents may change in concentration as the oil weathers, making it more difficult to identify the oil. Even in highly weathered oil, however, fingerprinting may still be useful in excluding other potential sources.

The primary weathering processes include spreading, evaporation, dissolution, dispersion, emulsification, and sedimentation. These processes occur for all discharges, but the rate and relative importance of each process depends on the specific oil and ambient environmental conditions. Exhibit C.3 illustrates the relative importance of these primary processes over time.

## Exhibit C.1

### GENERAL OIL PROPERTIES

#### **Type 1 Very Light Oils (Gasoline)**

- Highly volatile and soluble..
- Evaporates quickly, often completely within 1 to 2 days.
- High acute toxicity.

#### **Type 2 Light Oils (Jet Fuels, Diesel, No. 2 Fuel Oil, Light Crudes)**

- Moderately volatile.
- Will leave residue (up to one-third of spill amount) after a few days.
- Moderately soluble, especially distilled products.
- Moderate to high acute toxicity; product-specific toxicity related to type and concentration of aromatic compounds

#### **Type 3 Medium Oils (Most Crude Oils)**

- About one-third will evaporate within 24 hours.
- Typical water-soluble fraction 10-100 ppm.
- May penetrate substrate and persist.
- May be significant clean-up related impacts.
- Variable acute toxicity, depending on the amount of light fraction.

#### **Type 4 Heavy Oil (Heavy Crudes, No. 6 Fuel Oil, Bunker C)**

- Heavy oils with little/no evaporation or dissolution.
- Water-soluble fraction typically less than 10 ppm.
- Heavy surface contamination likely.
- Highly persistent, long-term contamination possible.
- Weathers very slowly; may form tarballs.
- May sink depending on product density and water density.
- May be significant clean-up related impacts.
- Low acute toxicity relative to other oil types.

#### **Type 5 Low API Fuel Oils (Heavy Industrial fuel oils)**

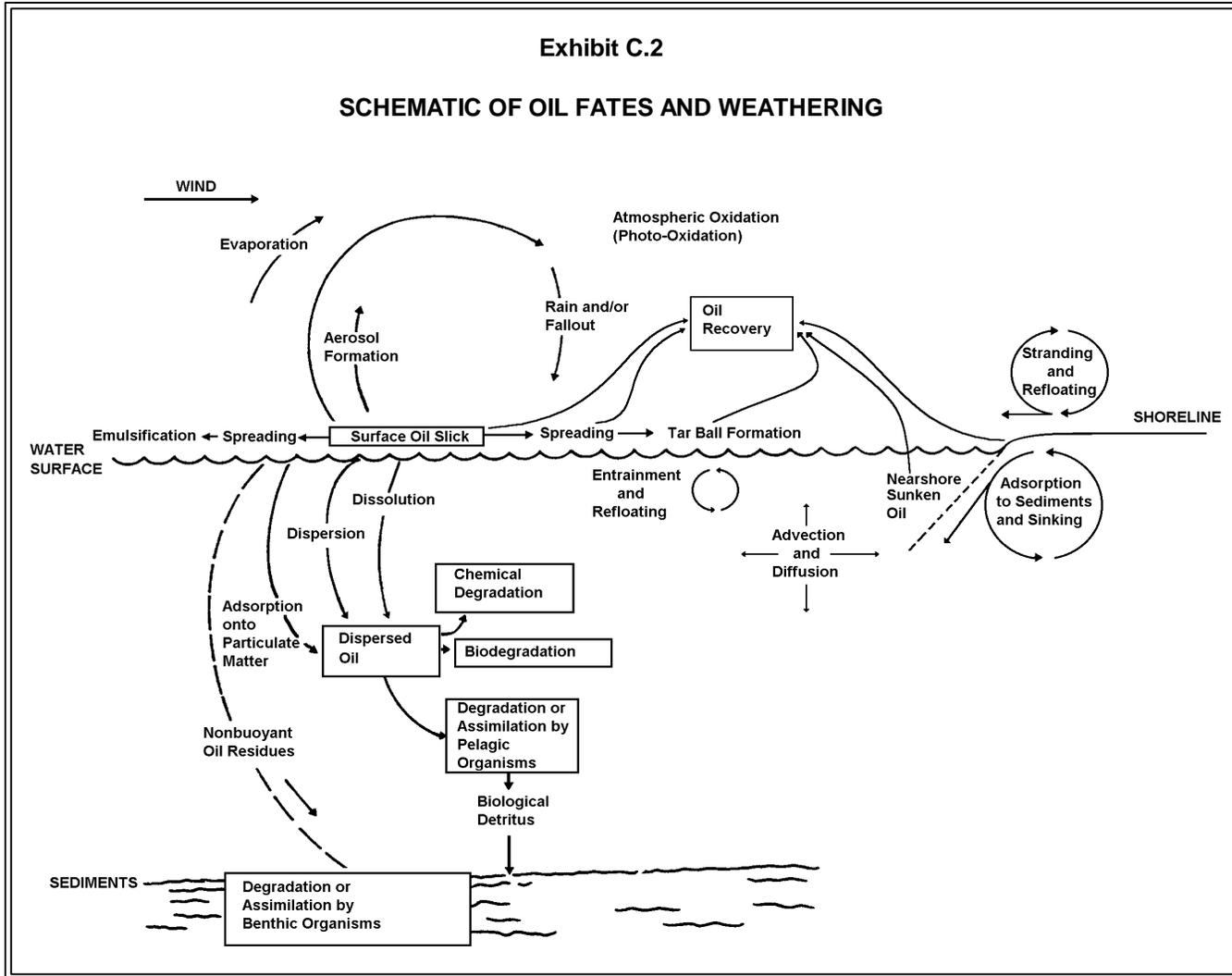
- Neutrally buoyant or may sink depending on water density.
- Weathers slowly; sunken oil has little potential for evaporation.
- May accumulate on bottom under calm conditions and smother subtidal resources.
- Sunken oil may be resuspended during storms, providing a chronic source of shoreline oiling.
- Highly variable and often blended with oils.
- Blends may be unstable and the oil may separate when spilled.
- Low acute toxicity relative to other oil types.

#### **Type 6 Animal and Plant Oils (Fish oil, vegetable oil)**

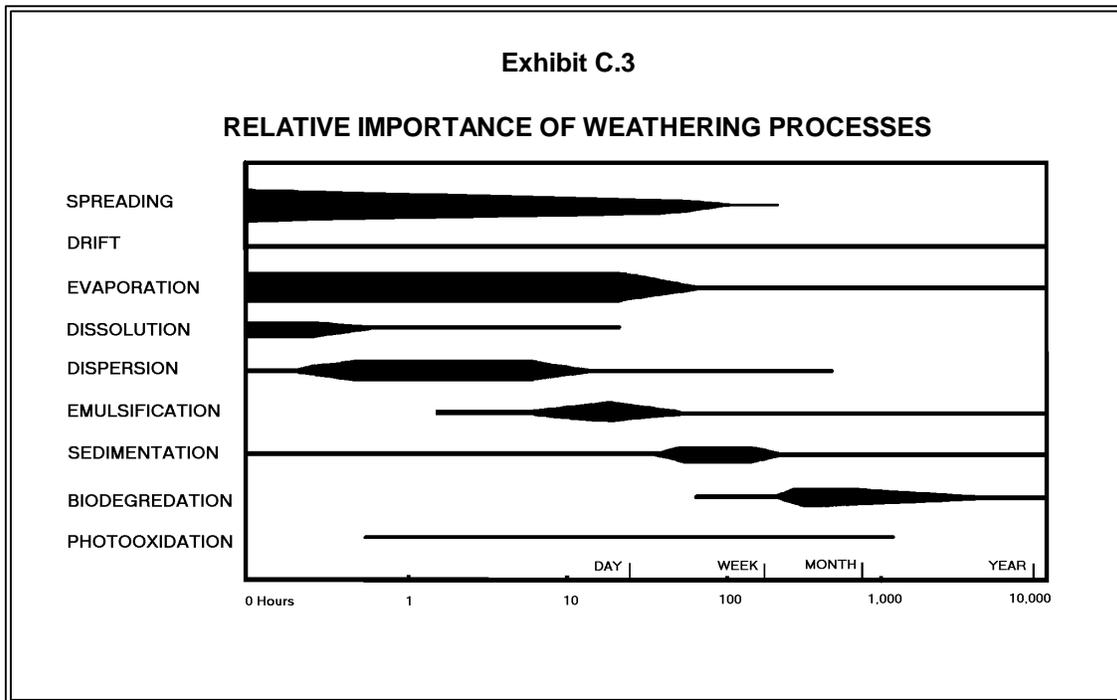
- Shipped in smaller quantities than petroleum oils, but may be stored in large quantities.
- Physical properties are highly variable.
- High biological oxygen demand (BOD), which could result in oxygen deprivation in confined water bodies.
- Low acute toxicity relative to petroleum oils.

Exhibit C.2

**SCHEMATIC OF OIL FATES AND WEATHERING**



Modified from National Research Council (1985)



From NOAA, 1992a

**Spreading:** As oil enters the environment, it begins to spread immediately. The viscosity of the oil, its pour point, and the ambient temperature will determine how rapidly the oil will spread, but light oils typically spread more rapidly than heavy oils. The rate of spreading and ultimate thickness of the oil slick will affect the rates of the other weathering processes. For example, discharges that occur in geographically contained areas (e.g., a pond or slow moving stream) will evaporate more slowly than if the oil were allowed to spread.

**Evaporation:** Evaporative processes begin immediately after oil is discharged into the environment. Some light products may evaporate entirely. A significant fraction of heavy refined oils also may evaporate. For crude oils, the amount lost to evaporation can typically range from approximately 20 to 60 percent (NOAA, 1992a). The primary factors that control evaporation are the composition of the oil, slick thickness, temperature and solar radiation, windspeed, and wave height. While evaporation rates increase with temperature, this process is not restricted to warm climates. For the *Exxon Valdez* incident, which occurred in cold conditions (March 1989), Wolfe et al. (1994) estimated that appreciable evaporation occurred even before all the oil escaped from the ship and that evaporation ultimately accounted for 20 percent of the oil.

**Dissolution:** Dissolution is the loss of individual oil compounds into the water. Many of the acutely toxic components of oils such as benzene, toluene, and xylene will readily dissolve into water. This process also occurs quickly after a discharge, but tends to be less important than evaporation. In a typical marine discharge, generally less than 5 percent of the benzene is lost to dissolution while greater than 95 percent is lost to evaporation (NOAA, 1992b). The dissolution process is thought to be much more important in rivers because natural containment may prevent spreading, reducing the surface area of the slick and thus retarding evaporation. At the same time, river turbulence increases the potential for mixing and dissolution.

**Dispersion:** The physical transport of oil droplets into the water column is referred to as dispersion. This is often a result of water surface turbulence, but also may result from the application of chemical agents (dispersants). These droplets may remain in the water column or coalesce with other droplets and gain enough buoyancy to resurface. Dispersed oil tends to biodegrade and dissolve more rapidly than floating slicks because of high surface area relative to volume.

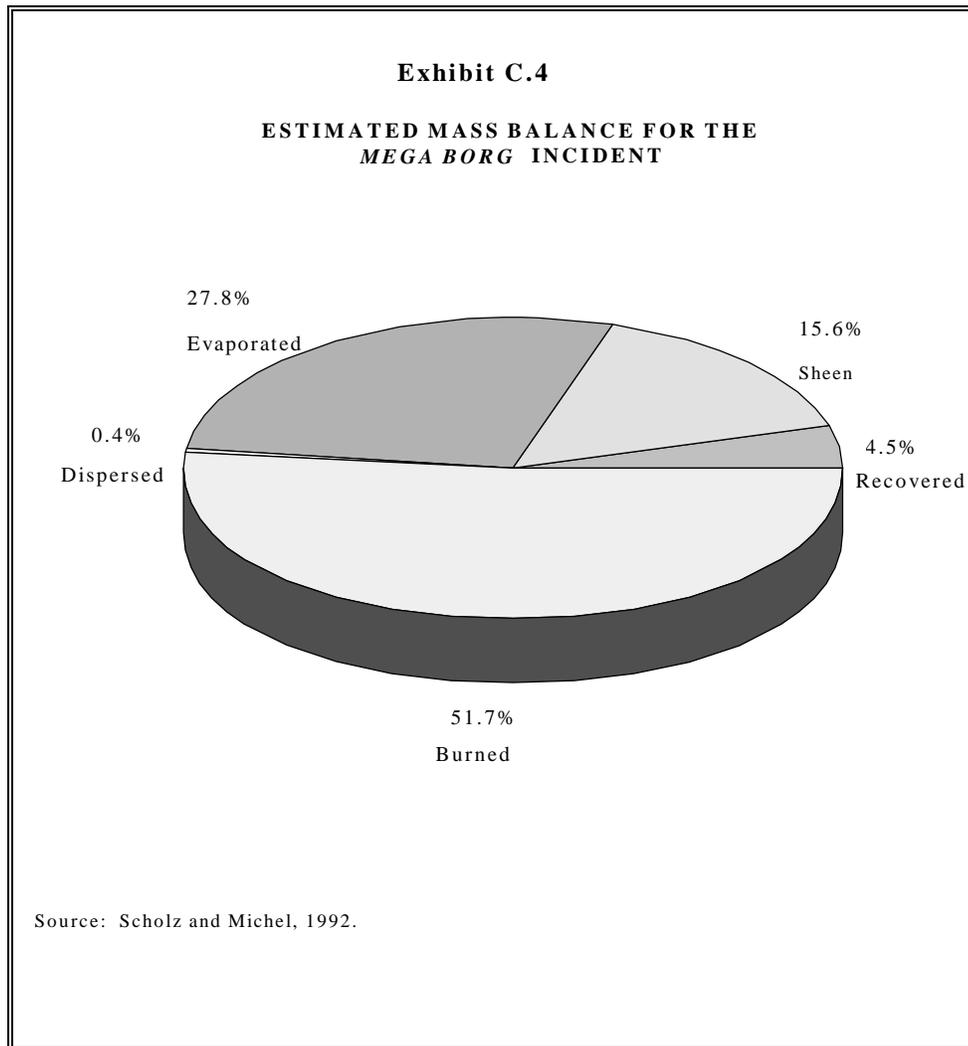
**Emulsification:** Certain oils tend to form water-in-oil emulsions or "mousse" as weathering occurs. This process is significant because, for example, the apparent volume of the oil may increase dramatically and the emulsification will slow the other weathering processes, especially evaporation. Under certain conditions, these emulsions may separate and release relatively fresh oil.

**Sedimentation or adsorption:** As mentioned above, most oils are buoyant in water. However, in areas with high suspended sediment levels, oils may be transported to the river, lake, or ocean floor through the process of sedimentation. Oil may adsorb to sediments and sink or be ingested by zooplankton and excreted in fecal pellets, which may settle to the bottom. Oil stranded on shorelines also may pick up sediments, refloat with the tide, and then sink.

**Other processes:** In addition to the primary weathering processes described above, there are several other processes that may be important to understanding the fate and potential for exposure. These include aeolian (wind) transport, photochemical degradation, and microbial degradation

## C.4 Mass Balance

One way to synthesize the overall fate of a discharge, including cleanup and weathering, is through the development of a mass balance. Although a detailed mass balance such as the one developed by Wolfe et al., (1994) for the *Exxon Valdez* incident may take several years to construct, a preliminary mass balance may be feasible during the Preassessment Phase. Consideration of the potential fates of the oil will assist trustees in estimating the loading of oil into certain habitats, which may be useful in identifying and scaling injury studies in certain areas. For example, Scholz and Michel (1992) conducted a mass balance on the *T/V Mega Borg* incident in Texas to determine the fate of the oil, including the fraction of the oil burned in the fire. This mass balance is illustrated in Exhibit C-4. This information was used in determining the potential for oil exposure to shrimp (Nance, 1992).



A mass balance also may be useful in evaluating the success of the response operations and provide a check on the total amount of oil discharged. A mass balance approach was used to check divergent estimates of a fuel oil discharge into the Cape Fear River, North Carolina (Baca et al., 1983). Mass balance estimates may be necessary if the trustees decide to use a model or compensation formulas, because these methods generally require an estimate of both the amount discharged and the amount recovered.

## C. 5 Pathways

To conclude that a specific injury resulted from a discharge, an exposure pathway linking the incident to the injury must be identified. Understanding the potential pathways will help to narrow the scope of the NRDA investigation, but also may be important in deciding which assessment methodology to use. For example, the Type A model does not address injuries that occur via air or terrestrial pathways. Note that injury determination does not require that natural resources be directly exposed to oil. An injury or loss of services can occur without the presence of oil. Therefore, an exposure pathway can be either:

- *Direct:* A sequence of events by which the oil traveled through the environment and physically came into contact with the natural resource. For example, direct oiling of a shellfish bed may result in mortality and decreased growth.
- *Indirect:* A sequence of events by which the effect of exposure to oil was transferred to the natural resource of concern, without the oil directly contacting the natural resource. For example, a decreased bait fish population caused by a spill may result in the starvation of a piscivorous bird, or a fishery may be closed to prevent potentially tainted fish from being marketed.

There are a number of potential exposure pathways. In some cases, these pathways may have multiple steps. For example, a common exposure pathway for birds is a surface water pathway, leading to physical exposure, leading to ingestion from preening. Although it is difficult to list all of the potential direct and indirect exposure pathways, several of the predominant pathways for discharges of oil are discussed below.

**Surface Waters:** Because most oils float, surface waters are often the exposure pathway of greatest concern. Surface waters may provide a pathway for exposure of open-water natural resources such as birds, mammals, and plankton in the surface microlayer; or a pathway to shoreline and intertidal natural resources. The surface waters themselves are a natural resource and floating oil may disrupt a number of natural resource services including recreation, transportation, and aesthetic values. This pathway is relatively straightforward to document using aerial overflights, surface vessel observations, and computer models designed to simulate the behavior and transport of surface oil slicks.

**Ingestion:** Ingestion is a common exposure pathway. Oiled birds will ingest oil during preening. Turtles feed on objects floating at the water surface, therefore they are susceptible to ingestion of tar balls, which can block the oral cavity and digestive tract (Van Vleet and Pauly, 1987). Injuries to river otters have been related to ingestion pathways, both from preening and from contaminated food (Bowyer et al., 1993). Ingestion pathways also have been observed for invertebrates. Christini (1992) noted that blue crabs were attracted to and ingested tarballs. Because many organisms can metabolize petroleum, biomagnification via trophic pathways is not considered an important pathway (McElroy et al., 1989; National Research Council, 1985), however, organisms may be exposed by ingesting contaminated prey (e.g., bioavailability). For example, bivalve mollusks such as mussels may accumulate petroleum hydrocarbons in their tissues and pass contamination on to higher trophic level predators such as birds or marine mammals. This pathway has been linked to the persistent reproductive failure of Harlequin Ducks in Western Prince William Sound following the *Exxon Valdez* incident (Patten, 1993). Approaches to studying ingestion and food web pathways include direct observation of feeding, preening behavior, and oiling of mouth parts; analysis of gut contents; tissue analysis of prey species; and feces analysis.

**Inhalation:** The potential for inhalation pathways depends on the volatility of the oil and degree of weathering. Inhalation pathways have been hypothesized to be important, especially to marine mammals. For example, following the *Exxon Valdez* incident, Frost and Lowry (1993) found central nervous system injuries and edema in harbor seals that was similar to that present in humans that die from inhaling solvents. Researchers postulate that killer whales were killed by exposure to volatile hydrocarbons after the *Exxon Valdez* incident (Dalheim and Matkin, 1993).

**Physical (Dermal) Exposure:** Surface water and other pathways may lead to direct physical exposure of a natural resource to oil. This contact may directly cause injury (e.g., smothering), may impair the physiology of the organism resulting in injury (e.g., hypothermia in birds and mammals from impaired thermoregulation), or may cause a service loss (e.g., dermal exposure in fish resulting in tainting). Direct contact through a dermal absorption pathway also may lead to contamination of organs, fluids, and tissues.

**Atmospheric:** The atmosphere may provide a pathway to natural resources or affect the service flows from these natural resources. The 1993 *Braer* incident in the Shetland Islands provides an example of an aeolian pathway. High winds carried the oil as a mist inland and contaminated approximately 20 square miles of crop lands, as well as oiling houses, cars, and a lake used for drinking water (Harris, 1995). Other less dramatic examples include the 1993 Colonial Pipeline incident in Virginia (Koob, 1995), where a break in a pipeline sprayed oil into the air and oiled a number of natural resources, including an upland forest area. The burning of oil (either deliberately or by chance) could increase atmospheric impacts. Atmospheric pathways may be especially important in determining the potential for lost use. For example, oil from the Colonial incident eventually flowed into the Potomac River, where odors resulted in the closure of Great Falls National Park and impairment of air quality along the Capital Mall area.

**Sediments:** Subtidal and intertidal sediments are an important pathway in most discharges, affecting biological resources, habitats, and service flows. In most instances, intertidal sediments are the primary pathway of concern, but extensive subtidal sediment contamination has been observed in a number of large incidents, such as the *Amoco Cadiz*, *Exxon Valdez*, *Braer*, and *Morris J. Berman*. Chronic exposure to oiled sediments has been correlated with reduced feeding, growth, and reproduction, and with histopathological changes in benthic fish. Sediment pathways also are important in recreational lost use. Beaches, for example, may be closed because of oiled sediments. Subtidal sediments may provide a pathway for chronic beach oiling (Burns et al., 1995).

**Groundwater:** Groundwater petroleum contamination can involve large amounts of oil and affect huge areas. One tank farm facility alone has been estimated to have released between 84 and 252 million gallons of petroleum into groundwater (Mould et al., 1995). Chronic groundwater contamination may result from leaking underground storage tanks or from chronic surface discharges (e.g., refineries, tank farms), while acute contamination may result from the sudden failure of storage tanks or other terrestrial incidents. Groundwater may provide a pathway for exposure to terrestrial and aquatic resources. In fact, many groundwater problems are first discovered when oil begins leaching into surface waters. Studying groundwater pathways generally involves the use of monitoring wells or sampling of existing drinking water wells in the aquifer.

**Water Column:** The potential for a significant water column exposure pathway depends on the dispersion and dissolution characteristics of the oil, response countermeasures, and ambient environmental conditions. Because of the ephemeral nature of water column exposure, studying water column pathways in-situ must be done quickly after a discharge and can be very costly. Alternatively, this pathway may be demonstrated based on literature information, laboratory studies on the physical behavior of the oil, or through the use of models

## C.6 Exposure

Demonstrating exposure is an important step in determining injury, but evidence of exposure alone is not sufficient to conclude that injury to a natural resource has occurred (e.g., the presence of petroleum hydrocarbons in oyster tissues is not in itself an injury). The purpose of the exposure portion of an injury assessment is to determine whether natural resources came into contact, either directly or indirectly, with the oil and to estimate the amount or concentration of the oil and the geographic extent of the oil. This information is necessary to design, interpret, and extrapolate the results of the injury studies.

A number of factors should be considered when formulating hypotheses regarding the potential for and significance of exposure.

**Oil Type:** The physical and chemical characteristics of the oil will strongly influence the potential for and nature of exposure.

**Spill Volume:** The size of the discharge will affect the nature of the exposure. During small discharges, for example, oil may concentrate in a band along the high tide line. The greatest potential for exposure may therefore occur at the high tide line and in detrital material. Under heavy accumulations, however, oil may cover the entire intertidal zone.

**Cleanup effects:** If oil is removed from the environment quickly before it comes in contact with sensitive natural resources, the potential for exposure will be greatly minimized. Response actions also may change the nature of oil exposure. For example, use of chemical dispersants will increase exposure to the water column. Increased sediment exposure may occur where machinery and foot traffic force oil into the substrate and equipment staging areas may also be severely impacted.

**Shoreline Type and Exposure:** The potential for exposure to oil varies with shoreline geomorphology and degree of exposure. In high energy areas, oil may be rapidly dispersed, generally reducing the potential for exposure. However, these same forces may result in oil being deposited above the high-water swash or buried by clean sand. Stranded or buried oil may be highly persistent. Oil exposure to rocky headlands may be minimal, but a sheltered beach a few meters away, where wave energy is less, may be heavily oiled.

In support of the NRDA regulations under OPA and for the purpose of facilitating the NRDA process under OPA, NOAA has produced a number of related guidance documents, in addition to the Preassessment Phase Guidance Document, that are relevant to preassessment activities. All of these documents are currently available in final form.

**Sediment Grain Size:** Oil holding capacity and the depth of penetration depends on sediment grain size. Oil will penetrate coarse-grained sediments much more rapidly and more deeply than fine sediments.

**Tide Stage:** For certain natural resources, the potential for exposure will depend on tidal height. Subtidal seagrass beds are generally less sensitive to oil discharges than intertidal plants, since they usually do not come into direct contact with the floating oil. Similarly, supratidal vegetation may be exposed to floating oil only on the highest spring tides.

**Weather Conditions:** Flood conditions or storm driven tides may strand oil in areas that would otherwise be immune from oiling. In freshwater systems, oil may be carried over stream or river banks and stranded in the flood plain. In open water, high winds and waves may break up some oils and minimize shoreline contamination. Weather conditions also can accelerate or retard oil weathering. Temperature can affect species presence and behavior and thus the potential for exposure to oil and injury.

**Behavior and Life History Considerations:** Animal behavior is a significant factor in the potential for exposure. For example, the feeding and roosting behavior of birds is a major factor in their potential for exposure to oil (King and Sanger, 1979). Certain life stages may be more vulnerable than others. Planktonic fish larvae have a greater potential for exposure because they tend to drift at the same rate as the oil, while adult fish may be able to avoid contaminants. Depending on the season, migratory birds and wildlife may be present and therefore at risk for exposure. Animals that aggregate during reproduction, such as certain marine mammals, birds, and fish, may be highly vulnerable.

**Duration of Exposure:** Time of exposure is a critical consideration in evaluating the potential for injury. A pelagic fish that is briefly exposed to oil while passing through a plume will be less likely to be injured than a fish that remains or is confined in the discharge area.

### **C.7 Approaches to Exposure Assessment**

Exposure is generally evaluated with a combination of quantitative and qualitative methods. As with other elements of the NRDA process, selection of appropriate strategies for determination of oil exposure will depend on the type and volume of discharged oil, natural resources at risk, nature of the receiving environment, and availability of personnel, funds, and equipment. A few of the potential approaches to evaluating exposure are described below.

**Computer Models:** Trajectory and weathering models may provide the first quantitative information on the fates of oil and the likelihood for exposure to specific natural resources and habitats. The NOAA On-Scene Spill Model (OSSM) is used to predict the short-term trajectory of the oil for response purposes, but also provides useful information for injury assessment (NOAA 1992b). Trajectory models are especially important if the trustees want to sample unoiled areas that are likely to be oiled later. The U.S. Department of the Interior's Type A models, Natural Resource Damage Assessment Model for Coastal and Marine Environments (NRDAM/CME) and Great Lakes Environments (NRDAM/GLE), also simulate the physical fates of spilled oils (USDIOI, 1994). The SAIC oil weathering model (Payne et al., 1983), and the NOAA ADIOS model (NOAA, 1994a) also predict the pathways and fates of specific oils. Models also may be useful in evaluating the potential for exposure in locations that are difficult or costly to sample, such as estimating subsurface hydrocarbon concentrations.

**Visual Observation:** Aerial and ground surveys provide a rapid tool for exposure assessment of large areas. This approach is especially useful in documenting the overall distribution of oil-induced injuries by habitat or region, as well as identification of potential reference and impact areas. The qualitative and semi-quantitative information collected in this manner is generally combined with more detailed ground surveys and oil sampling to confirm exposure. Observations generally include estimates of the width, length, area, and degree of contamination in each affected habitat. General guidance on conducting and interpreting aerial and shoreline surveys can be found in NOAA (1992a,b); NOAA (1994c); Owens (1991); Environment Canada (1992); and Michel et al., (1994). Visual observation also may be used to determine the presence of oil on vegetation and individual organisms.

**Presence of Oily Odor:** Exposure to oil may also be evaluated qualitatively through organoleptic testing, the sensory evaluation of tainting using taste and smell (Ackman and Heras, 1992; Tidmarsh and Ackman, 1986; NOAA, 1994d). This was one of the approaches used in the *Exxon Valdez* incident to determine if commercially caught fish had been exposed to oil (Walker and Field, 1991). The ability to detect oils by smell will vary with the chemical composition of the oil, degree of weathering, and sensitivity of the individual. Low molecular weight oil components tend to be the easiest to smell, while the high molecular weight oil components, which may be of the greatest concern for possible long-term effects, are less volatile and thus harder to detect. The high variability of crude and fuel oils makes it difficult to characterize individual products by their odor threshold, but the USCG Chemical Hazards Response Information System (CHRIS) database lists the odor threshold for several petroleum products, including gasoline at 0.25 ppm, kerosene at 1 ppm, and Jet fuel (JP-5) at 1 ppm (Weiss, 1980).

**Body Burden:** Exposure to oil can be evaluated with a suite of analytical chemistry techniques ranging in cost, selectivity, and sensitivity. The choice of the method(s), analytes, and detection limits should be made by the NRDA team, in concert with their analytical laboratory, and should depend on the circumstances of the discharge, the type of sample, the required sensitivity, the degree of sample degradation, metabolism, and weathering, and whether quantitative or qualitative information is necessary. Chemical analyses for fingerprinting, for example, may provide information on the type and degree of weathering of the oil, but generally will not provide an estimate of the concentration of the contaminant in the sample matrix. However, both fingerprinting and determination of contaminant concentrations can be accomplished simultaneously, depending upon how the sample is collected. A detailed discussion of the various analytical methods used in petroleum chemistry is beyond the scope of this document, but the basic approaches are outlined below. For more information on oil chemistry and analysis, the reader should refer to Burns (1993); Sauer et al. (1993); Duckworth and Perry (1986); Boehm et al. (1995); Sauer and Boehm (1991); and McAullife et al., (1988). Trustees also may review PTI (1992) for general guidance on selecting chemical analyses.

There are three major objectives for the chemical analysis of oil, and different analytical methods may be necessary to accomplish these objectives. The three objectives are:

- *Physical and chemical characterization* of the oil, including major constituents, to provide information on how that oil will behave in the environment, its potential fates, persistence, toxicity, and carcinogenicity, and to identify target analytes for fingerprinting;
- *Fingerprinting* to determine whether the oil in an environmental sample is from the specific incident, or from another source of oil pollution; and
- *Concentration* to determine the quantity of the oil or important constituents of the oil in environmental samples.

**Presence of Oil in Transplanted Bivalves:** Bivalves such as clams, mussels, and oysters can be used as indicators of exposure and bioeffects. They provide integrated information about the bioavailability and effects of oil that cannot be determined solely through the chemical analysis of discrete water samples. This capability is particularly important in monitoring oil discharges where exposure can be highly variable. The uptake of the discharged oil by bivalves is evidence of exposure to the bivalves themselves as well as an indication of exposure for other injured natural resources. Bivalve collection and procedures for chemical analysis of tissues have been standardized as part of the National Status and Trends Program (NOAA, 1989) and guidelines for using transplanted mussels in NRDA studies are summarized in Salazar (1992) and Michel et al. (1994). Mehl and Kocan (1993) have developed methods to estimate the exposure concentration of the seawater soluble fraction of crude oil from the tissue concentrations in caged mussels deployed after discharges.

**Surrogate Samplers:** Water column and sediment exposure may be integrated over time through the use of surrogate samplers, such as semi-permeable membrane devices (SPMDs) or lipid bags (Lebo et al., 1992; Crecelius and Lefkovitz, 1992; Crecelius et al., 1994).

**PAH Metabolites:** Many oil components including benzene and polycyclic aromatic hydrocarbons (PAHs) are rapidly metabolized by aquatic organisms and do not tend to accumulate in tissues. For vertebrates, documentation of exposure to petroleum hydrocarbons may be complicated. However, the metabolites of PAH compounds can be detected, especially in bile, even though the parent compound may no longer be detectable (Varanasi et al., 1989). Presence of these metabolites is an indication that the organism has been exposed to PAHs, but it may be difficult to determine the exact source of that exposure.

**Mixed Function Oxygenase (MFO) Enzymes:** Certain organisms possess enzyme systems that can detoxify contaminants. The most important enzymes in the detoxification process are known as MFO enzymes. The activity of these enzymes is evidence that the organism has been exposed to contaminants (Payne et al., 1986; Collier and Varanasi, 1991). However, interpretation of enzyme activity level is complicated because other stresses can lead to elevated levels, so other exposure data may be necessary to confirm that the elevated levels are associated with the contaminant of concern (McDonald, 1992).

**Hemolytic Anemia:** The decreased concentration of red blood cells and/or hemoglobin has been used as an indicator of oil exposure in certain vertebrates. Birds that have been exposed to oil may develop anemia within days (Leighton, 1982). Sea otters exposed to oil from the *Exxon Valdez* incident also developed anemia (Williams, 1990).

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